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LA-UR--83-2241

DE83 015215

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ALPHA AND BETA - O₂ AS A FUNCTION OF PRESSURE

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SUBMITTED TO IX AIRAPT Conference, Albany, NY, July 24-29, 1983.

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CALCULATION OF STRUCTURES AND MAGNETIC ORIENTATIONS IN SOLID α - AND β -O₂
AS A FUNCTION OF PRESSURE[†]

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ABSTRACT

An optimization method is coupled with a harmonic lattice-dynamics approximation to determine the minimum energy structures and magnetic orientations of solid O₂. It is shown that the magnetic interaction is responsible for the stability of α -O₂ with respect to β -O₂ at zero temperature and pressure. The calculated α -O₂ lattice parameters, magnetic orientations, and sublimation energy are in good agreement with experiment. Phonon dispersion curves are calculated and the acoustic sound velocities are determined. The β -O₂ phase is described by constraining the magnetic moments so that the magnetic Hamiltonian preserves the hexagonal symmetry of the crystal. The calculated lattice parameters are in good agreement with experiment and a three-sublattice, quasi-helical magnetic orientation is predicted from structural and energetic considerations. A soft mode induced phase transition from the monoclinic α structure to the orthorhombic orange oxygen structure is predicted at approximately 6 kbar. No volume change is observed at the transition. The pressure dependence of the intramolecular stretching mode is also calculated and it is shown to exhibit very little dispersion.

INTRODUCTION

Oxygen is unusual in that it embodies both the properties of a molecular solid and a magnetic material. The magnetic character results from two unpaired p shell electrons in the molecule, giving it spin $S = 1$. The lowest temperature phase at zero pressure forms a monoclinic C2/m structure, [1] often called α -O₂, where the molecular axes are collinear and normal to the close packed basal plane, as defined by the lattice vectors a , b on Fig. 1a. The magnetic moments are known to be collinear and perpendicular to the molecular axes.[2] The arrows on Fig. 1a show the magnetic moment directions, which give rise to an antiferromagnetic structure.

At zero applied pressure and $T=23.8$ K, a phase transition occurs into the rhombohedral R $\bar{3}m$ β -O₂ structure.[3] The highest-density plane is hexagonal with a three-layer repeat pattern. This plane and the next two layers, identified by crosses and zeros, are shown in Fig. 1b. The molecular axes lie along the c axis perpendicular to the hexagonal plane.

Experimental information about the magnetic properties of β -O₂ gives a somewhat conflicting picture.[4-6] The magnetic susceptibility is more antiferromagnetic in character than paramagnetic[6-8] However, the neutron scattering work of Collins [2] shows little evidence of long-range

[†] Work supported by US Department of Energy and NATO Grant No. 132-80.

antiferromagnetic order even though there are some unexplained features in the spectrum.[4-5] As a consequence of the experimental situation, $\beta\text{-O}_2$ has been predicted to be either paramagnetic or to have short range antiferromagnetic order.[4,6,7] Recent experiments even suggest the possibility of long-range order.[8] Another prediction [7] postulated to help explain several features of O_2 in the vicinity of the α - β transition is that the magnetic moments reorient from the colinear α arrangement into an orientation in which all nearest neighbors are at $2\pi/3$ with respect to one another. This rearrangement is supposed to occur in a narrow temperature interval around that transition and then persist into the β phase. The basal-plane arrangement is shown by arrows in Fig. 1b.

Another phase that has recently been observed [9] is the orthorhombic $Fmmm$, "orange" oxygen structure. The molecular axes appear to be colinear and normal to the ab plane. It has been observed over a temperature range $240 < T < 300$ K at pressures $70 < P < 100$ kbar. It is not known how low in temperature and pressure this phase persists. The phase diagram for O_2 is shown on Fig. 2, where the solid lines are fairly well established and the dashed lines are tentative.

Previous calculations [10-13] have failed to predict the observed low temperature stability of the α phase over the β -phase and it has been conjectured that the reason for this failure is the lack of a magnetic interaction in the total potential. Therefore, our task has been to construct a potential of the following form.

$$U_T = U_g + U_{\text{intra}} + U_m \quad (1)$$

$$U_m = -2 \sum_{i < j} J(R_{ij}) \hat{S}_i \cdot \hat{S}_j \quad (2)$$

and $J(R_{ij})$ is the exchange energy between two molecules with center of mass separation R_{ij} and \hat{S}_i is a unit vector specifying the direction of the magnetic moment of molecule i . The anisotropic terms neglected in U_m

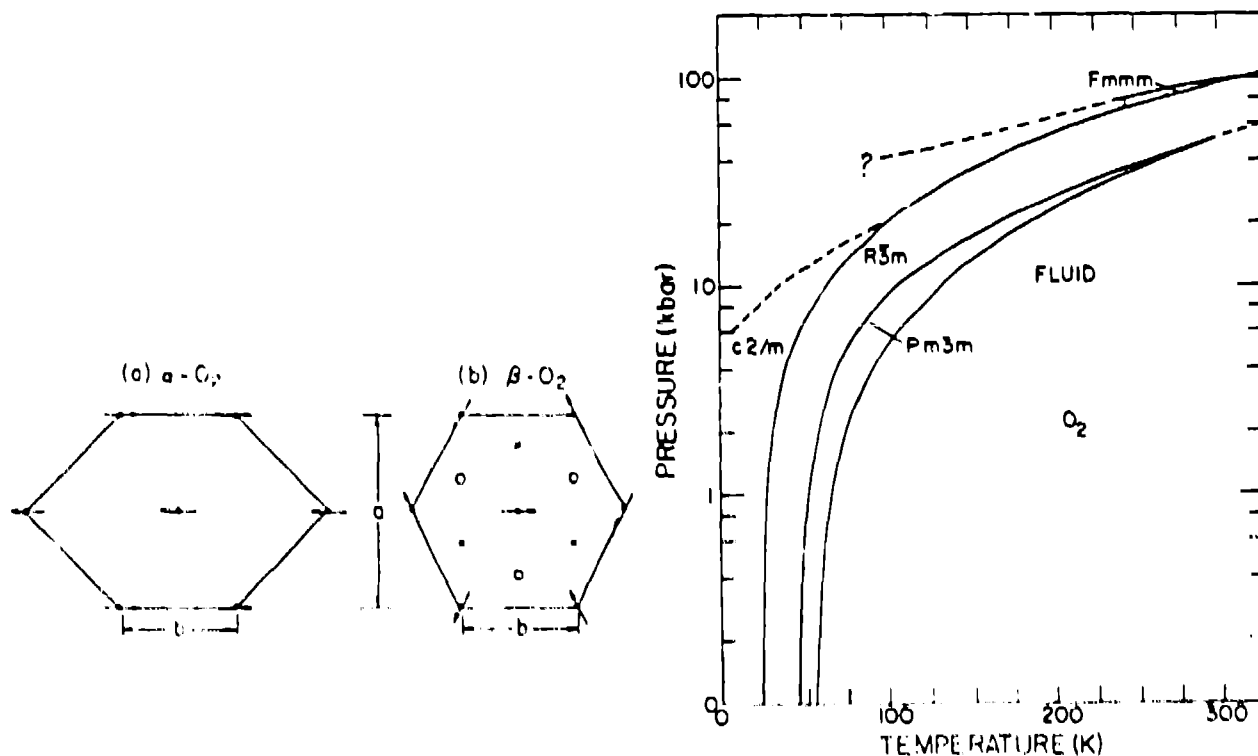


Fig. 1. Basal planes for α and $\beta\text{-O}_2$. Fig. 2. Phase diagram for O_2 .

make negligible contributions to the crystal energy and structures, but they are important in establishing the direction of the magnetic moments with respect to the crystal body axis. [6,7,14] This feature is described here by applying constraints on the $\{S_i\}$. For J, we have used recent magnetic susceptibility data [8] taken over pressures $0 < P < 6$ kbar. It takes the form $J(R) = J_0 \exp[-\alpha(R-R_0)]$, where $\alpha = 4.3 \text{ \AA}^{-1}$, $R_0 = 3.2 \text{ \AA}$, and $J_0 = 28.25 \text{ K}$, which is determined from the observation [8] that the value of J at nearest neighbor separation R_{nn} is $J(R_{nn}) = 36 \text{ K}$. The intramolecular potential U_{intra} is expressed by the quadratic and cubic terms in a Taylor series expansion about the gas phase equilibrium bond length. [15]

In the paramagnetic gas phase the expectation values $\langle U_{\text{intra}} \rangle$ and $\langle U_{\text{m}} \rangle$ equal zero so the total potential $U_T = U_g$. Thus U_g is the gas phase potential and the following atom-atom form has been adopted.

$$U_g = \sum_{i < j}^N \sum_{s=1}^4 \{ A \exp [-\alpha r_s(i,j)] - B/r_s^6(i,j) \} + U_{\text{EQQ}} \quad (3)$$

where $r_s(i,j)$ is the distance between non-bonded atoms of molecules i and j. U_{EQQ} is the electric quadrupole - quadrupole interaction. A point charge model is used to describe this interaction where the distance between charges on the molecule is adjusted to yield the observed quadrupole moment. [16] The parameters α , A, and B have been determined to yield a best overall fit to the second virial coefficients [17] and molecular beam scattering data. [18] The values of the parameters (α, A, B) determined in this way are (3.68 \AA^{-1} , 1120.6 eV , 12.91 eV \AA^6). Thus, solid properties will be determined from a potential derived from only gas phase and susceptibility data, and it is otherwise unadjusted.

III. Method

The total potential energy U_T is evaluated using a pattern search optimization scheme which minimizes the energy with respect to all the independent lattice parameters, including the intramolecular separation d. These parameters are then used in a harmonic lattice-dynamics calculation and the quantum mechanical expectation value of the Hamiltonian, including zero-point contributions, is evaluated. The lattice parameters are then isotropically varied until the free energy is minimized. A new pattern search is initiated at this volume and new lattice parameters are determined. With these lattice parameters a new lattice-dynamics calculation is initiated and the free energy is minimized with respect to the volume. This procedure is continued until convergence is reached, generally after one iteration. At pressures $P \neq 0$, the same procedure is used subject to the constraint of a specific volume. Details of the optimization scheme are given elsewhere [19] and lattice sums are taken out to 12 \AA .

RESULTS AND DISCUSSION

A free variation of the lattice parameters a, b, c, β , and the intramolecular separation d at $T=0$ shows that the minimum-energy configuration is the monoclinic $\alpha\text{-O}_2$ structure. To test for stability the initial structure used in the pattern-search optimization of U was widely varied and $\alpha\text{-O}_2$ was invariably predicted as the lowest-energy structure.

The calculated zero pressure equilibrium volume, lattice parameters and binding energy E, i.e. $(V, a, b, c, \beta, E) = (21.06 \text{ cm}^3/\text{mole}, 3.24 \text{ \AA}, 3.49 \text{ \AA}, 5.03 \text{ \AA}, 130.5^\circ, 1022 \text{ K})$, compare favorably to the experimental values [20] of $(20.81 \text{ cm}^3/\text{mole}, 3.375 \text{ \AA}, 3.42 \text{ \AA}, 5.065 \text{ \AA}, 132.18^\circ, 1042 \text{ K})$. The nearest neighbor distance is 3.15 \AA compared to the experimental value of

3.186 Å. β is the angle between \underline{a} and \underline{c} . These results show that the magnetic interaction is responsible for distorting the basal plane of O_2 from the hexagonal symmetry associated with the β structure, because it is known that the other terms in Eq. (1) cannot break that symmetry.

For β - O_2 , calculations were performed for a variety of magnetic structures where U_m does not break the known hexagonal symmetry. Results based upon the assumptions that β - O_2 is either paramagnetic or in the quasi-helical structure, shown in Fig. (1b.), are as follows. For the paramagnetic case at the experimental volume of $21.02 \text{ cm}^3/\text{mole}$ at $T = 23.8\text{K}$, the results for the lattice parameters (b , c) are (3.267, Å, 11.342 Å) and, based upon the quasi-helical structure they are (3.24 Å, 11.54 Å), compared with the experimental results [20] of (3.272 Å, 11.295 Å). Moreover, the system properly relaxes into the rhombohedral β - O_2 structure. Clearly, both of these possible magnetic arrangements give good predictions for the structure and the lattice constants. Of all the magnetic orientations investigated the quasi-helical structure gives the lowest energy. On the basis of this and the strength of the magnetic interaction we predict that the quasi-helical structure, with long range antiferromagnetic order, is the most probable state of β - O_2 . Recent spin polarized neutron scattering results [21] seem to corroborate that prediction.

The calculated isothermal compressibility at $T = 0\text{K}$ and low pressure is $K = 2.6 \times 10^{-11} \text{ cm}^2/\text{dyne}$, compared to the experimental data [20] extrapolated to zero temperature of $K_{\text{exp}} = 2.76 \times 10^{-11} \text{ cm}^2/\text{dyne}$. The calculated pressure is displayed by the solid line on Fig. 3. Keeping in mind that this is a zero temperature isotherm, only the experimental data points designated by the square [22] and the triangle [20] are at sufficiently low temperature to ignore thermal expansion [23]. These points agree quite well with the calculation. The circles represent the experimental data of Stewart [24] at $T = 51\text{K}$. To compare that data with our $T = 0$ isotherm an approximate thermal pressure P_T was calculated.

The dashed line represents our calculated $T = 51\text{K}$ isotherm, determined using P_T . Up to $P = 6 \text{ kbar}$ the results are in good agreement with Stewart's data [24] but the curve falls increasingly below experiment as the pressure is increased. It is not clear whether this discrepancy is a consequence of the highly approximate determination of P_T or due to a deficiency in the potential U_T . It is apparent, however, that the results are an improvement over those calculated from the English-Venables potential, [13] which is shown by the dot-dashed line for the $T = 51\text{K}$ isotherm. Figure 4 shows the zero pressure dispersion curves, where L_a and L_b denote librational modes about the a and b axes, respectively. Similarly T_i , ($i = a, b$, or z) designates translational vibrations along the i axis. The dispersion of the internal O_2 stretch mode is not shown but it is essentially flat, with a decrease of approximately 1.5 cm^{-1} from zone center to zone edge at $P = \text{zero}$, and about 10 cm^{-1} at $P = 70 \text{ kbar}$. This is consistent with the notion that the high frequency stretch mode is essentially decoupled from the much lower acoustic and libron modes. The zero pressure dispersion curve shown on Fig. 4 is quantitatively different from the earlier work of Kobashi, et al. [10] because of the magnetic interaction in our model and because our crystal structure is totally relaxed and in equilibrium. One feature we do have in common with several previous calculations [10,25,26] is that the two $k = 0$ librational modes have nearly the same frequency (46 and 52 cm^{-1}). The observed Raman bands at 44.5 and 79 cm^{-1} were assigned to the L_a and L_b modes, respectively. For several reasons elucidated by previous workers [28] we believe these assignments are not

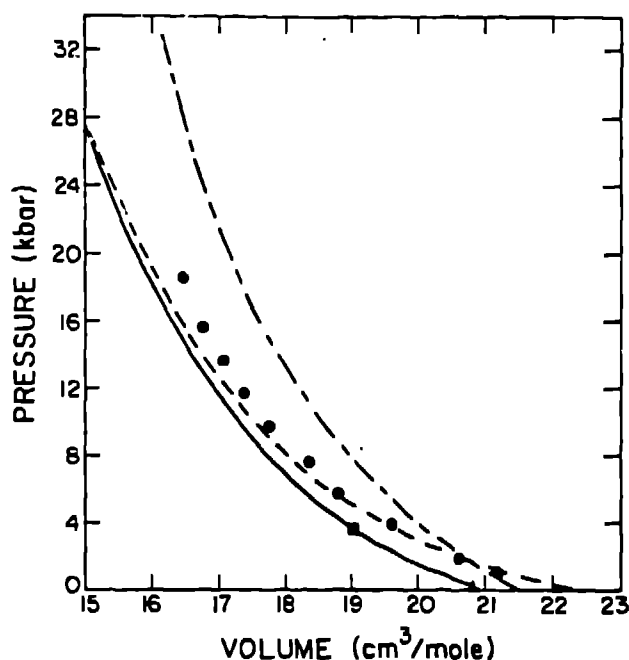


Fig. 3. Pressure volume curve for solid O_2 .

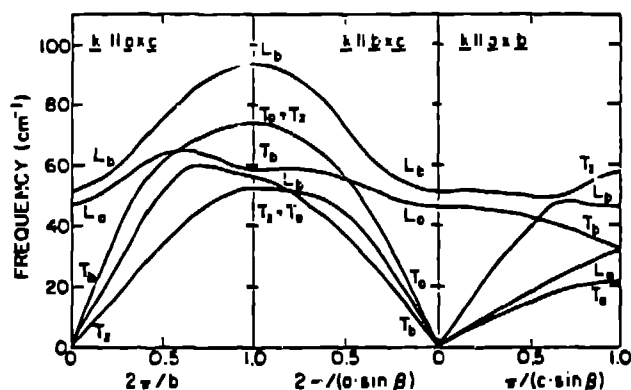


Fig. 4. Dispersion curves for α - C_2 .

degenerate and the one at 79 cm^{-1} is probably a two libron band. The acoustic sound velocities at $P = 0$ for the T_a , T_b , and T_z modes, respectively, are (1.2, 1.5, 0.75 km/sec), (1.6, 1.6, 1.2 km/sec), and (1.0, 0.9, 2.0 km/sec) for $\vec{k} \parallel \vec{a} \times \vec{c}$, $\vec{k} \parallel \vec{b} \times \vec{c}$, and $\vec{k} \parallel \vec{a} \times \vec{b}$, respectively.

The dispersion curves at higher pressures are qualitatively similar to those at $P = 0$ and the frequencies scale upward nearly uniformly with pressure. However the transverse acoustic shear mode T_a with propagation vector \vec{k} perpendicular to the ab plane shows a softening from $0 < P < 6$ kbar, where normal behavior with pressure commences.

Soft mode behavior suggests the possibility of a phase transition and an angle β' can be defined for the monoclinic structure which becomes orthorhombic when $\beta' = \pi/2$. In this work β' decreases rapidly with pressure to a value of $\pi/2$ at 6 kbar where it remains to the highest pressures calculated. This behavior in addition to the soft mode and the noticeable change with pressure in the lattice parameters near 6 kbar clearly show that a monoclinic to orthorhombic phase transition occurs near $P = 6$ kbar. An investigation of the P - V results shows no volume change or other evidence of the transition. This is not surprising since the transition is effected by a simple shear. We therefore speculate that the phase change is not first order. The structure and molecular orientations of this new phase are same as the $Fmmm$ "orange" structure which has been observed [9] at high pressures and temperatures, as shown in Fig. 1. It is therefore natural to assume that this predicted new phase is just the continuation of the observed "orange" oxygen phase down to low temperatures and pressures.

The authors wish to express their appreciation to R. L. Mills, B. Olinger, D. Schiferl, E. LeSar, and J. W. Shaner for very helpful discussions about the experimental data and its relation to this work.

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